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Oxygen Barrier Coatings for Enhanced Stability of Polyimide Composites at Elevated Temperatures

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submitted by

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I. INTRODUCTION

Polyimides are an important class of materials which can be used as the matrix material in carbon fiber reinforced composites. Polyimides have already found extensive application in space exploration, and the most well known trademark, Dupont Kapton®, is currently planned to be used as the solar cell mount for the space station solar array. The maximum service temperature of conventional polyimides is about 350°C. At higher temperatures (to 450°C), in an ambient air environment, conventional polyimides undergo oxidative degradation, rendering them useless as structural materials at these temperatures. The focus of the work to be discussed here was to explore new ways to improve the oxidation resistance of polyimide-based composites (PBCs) in higher temperature applications, and the approach is to use thin film coatings to prevent oxygen contact with the polyimide surface.

Chemical vapor deposition (CVD) has been chosen as the method for deposition of the protective thin film onto the composite surface. The primary advantages of the CVD technique are its ability to prepare a large variety (metals, ceramics) of coatings and to provide, in some cases, conformal coverage over an irregularly shaped or rough surface, such as might be encountered at the surface of a composite material.

In this work, we have examined the use of oxide coatings (SiO_2 and Al_2O_3) as oxygen barrier coatings for PBCs. The work began with an investigation of the use of ion implantation to improve the adhesion of SiO_2 to the PBC surface. That study is reported in Section II. In Section III, SiO_2 was looked at as an oxidation barrier. In Section IV is reported our study of the use of two dissimilar materials (SiO_2 and Al_2O_3) as oxidation barriers on PBCs. In Section V, we discuss our current and future work in this area.

II. ION IMPLANTATION STUDY

II.A. Background

In this study, a thin film (500-5000 Å) of silicon dioxide was deposited by plasma-enhanced chemical vapor deposition (PECVD) over the composite surface as a protective coating. With silicon in its highest oxidation state (+4), SiO_2 is resistant to high temperature oxidation. An important consideration is the adhesion of the SiO_2 film to the composite surface. To improve adhesion, the technique of ion implantation was utilized. An energetic beam of He^{2+} ions produces a combination of nuclear and electronic energy displacement in order to facilitate better adhesion of the film. The effect of implantation energy, dose, and film deposition parameters were investigated.

The thermodynamic criteria of good adhesion between the two surfaces of materials A and B, with no interdiffusion of atoms or ions, is that the sum of their individual surface energies (γ_A and γ_B) should be greater than the free energy of the interface, γ_{AB} . The adhesive energy, E_D , is then obtained as follows:

$$E_D = \gamma_A + \gamma_B - \gamma_{AB}$$

Therefore, to maximize the adhesive energy, the free energy of the interface should be minimized. However, there are many factors, such as atomic disorder, dislocations, and thermal and mechanical stresses, which can increase the free energy of the interface. Under conditions such that the atoms at the interface are given an opportunity to enter into interatomic bonding, the free energy of the interface is reduced.^{1,2} The chemical vapor deposition technique generally results in chemical bonding between the film and substrate and thus is attractive for this application.

To further enhance adhesion, post-deposition ion implantation can be useful. As an energetic ion passes through a material, it loses energy by two separate processes. In one process, atoms in the material are displaced through direct collisions, which is referred to as nuclear energy loss. In the other process, energy is deposited into the electronic structure of the substrate material, and this process is referred to as electronic energy loss. When an energetic particle passes through an interface, both forms of energy can occur, and the magnitude of each depends on the ion energy and mass and atomic number of the ion and the masses and atomic numbers of the atoms adjacent to the interface. By choosing ion beams which deposit most of their energy in electronic energy loss at the interface, it is possible to affect the chemistry of the interface so as to improve adhesion. Much has been published in this area covering a wide range of examples of improved adhesion in metal-nonmetal and nonmetal-nonmetal systems.^{3,4,5} Of particular relevance is work of Horwath, et al.⁶ who demonstrated that the adhesion of copper to polyimide could be enhanced by bombardment with 1.5 MeV helium or 3 MeV neon at fluences which would not cause significant levels of displacement damage and hence carburization of the polymer.

The Ohio University accelerator is well suited to fundamental studies of the effects of MeV helium or proton ion beams on ion enhanced adhesion of interfaces. It can generate proton beams of 1.4 to 9.0 MeV with beam currents of up to 20 μ A and helium beams of 2.2 to 13.5 MeV with currents up to 0.5 μ A.

¹J. S. Colligon and H. Kheyrandish. Vacuum, **39** 705 (1989).

²A. C. Adams and C. D. Capio. J. Electrochem. Soc. **126** 1042 (1979).

³T. A. Tombrello. Mat. Res. Soc. Symp. Proc. **25** 1 (1984).

⁴J. E. E. Baglin, G. J. Clark, and J. Bottinger. *ibid*, p. 179.

⁵I. V. Mitchell, J. S. Williams, D. K. Sood, K. T. Short, S. Johnson, and R. G. Elliman. *ibid*, p. 189.

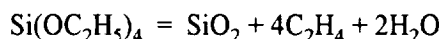
⁶R. S. Horwath, R. L. Headrick, and J. W. Wilson. Proc. Int. Ion Eng. Congress. Kyoto, (1983), p. 1743.

In the present study, a stoichiometric SiO₂ film was deposited on the composite surface from an organosilicon precursor (tetraethylorthosilicate) by plasma-enhanced chemical vapor deposition (PECVD).^{7,8,9,10} Several samples were ion implanted in an attempt to improve adhesion. The effect of high temperature (to 450°C) on the coated surface was also investigated.

II.B. Experimental Procedure

The deposition of SiO₂ films on the polyimide composite surface was performed in a PECVD reactor, which consisted of a process chamber with a capacitively-coupled radio frequency generator (13.56 MHz). In addition to rf power, an electrically powered substrate heater was also provided. The process chamber was evacuated by means of a mechanical pump. The portion of the process chamber surrounding the substrate heater was constructed of copper and was cooled by water circulating in coils brazed to the outside of the chamber walls. Critical process parameters, including substrate temperature, reactor pressure, RF power, and carrier gas flow rate, were monitored and controlled for process characterization. A schematic diagram of the deposition system is shown in Figure 1.

The pyrolytic, plasma-induced decomposition of tetraethylorthosilicate (TEOS) occurs through a heterogenous reaction which takes place at the composite surface. The reaction can be represented in an overall stoichiometric equation as¹¹



The overall process can be considered as a sequence of the following physico/chemical steps: 1) forced flow of the reactant in vapor form with the carrier gas (argon) into the system, 2) diffusion of TEOS toward the composite surface, 3) adsorption and decomposition of the reactant species at the surface, and 4) desorption and diffusion of the product gases from the surface to the bulk gas.

II.C. Results and Discussion

Deposition parameters for the PECVD process are listed in Tables I and II. Film thicknesses (and hence deposition rates) were measured by placing a witness sample consisting of a piece of Si wafer in the

⁷S. Rojas, A. Modelli, W. S. Wu, F. Santarelli, A. C. Sarti, and F. Minni. J. Vac. Sci. Technol. **B8** 1177 (1990).

⁸F. S. Becker, D. Pawlik, H. Anzinger, and A. Spitzen. J. Vac. Sci. Technol. **B5** 1555 (1987).

⁹B. L. Chin and E. P. Van de Ven. Solid State Technol. **31** 119 (1988).

¹⁰F. S. Becker and S. Rohl. J. Electrochem. Soc. **134** 2923 (1987).

¹¹S. Rojas, P. Serra, W. S. Wu, F. Santarelli, A. C. Sarti, and F. Minni. J. Physics **50** 83 (1989).

chamber adjacent to the substrate of interest. A portion of this witness sample was masked with a second piece of silicon during deposition. Afterward, the mask was removed and the resulting step profiled with a Sloan Dektak® Model IIA surface profilometer. Direct measurement of film thickness on those samples subsequently studied by Rutherford Backscattering Spectroscopy (RBS) confirmed the values obtained from this witness technique. The stoichiometry of the films was analyzed by RBS. The Si:O ratio was found to be 1:2, with less than 3% hydrogen as the only impurity for all films deposited under the process conditions listed in Table II.

The highest rate of deposition achieved was 175 Å/min, and the range of film thicknesses obtained was 500 Å to 5000 Å. Film uniformity was calculated from five separate measurements in different locations on the silicon wafer witness samples. The film thickness variation across the wafer was calculated as follows:

$$\text{Variation } (\pm\%) = 100(D_{\max} - D_{\min}) / (D_{\max} + D_{\min})$$

where D_{\max} and D_{\min} are the maximum and minimum film thicknesses, respectively.

Fourier transform infrared spectroscopy (FTIR) over the spectral range 400-4000 cm^{-1} was also utilized to reveal the bonding structure in the deposited films. A strong absorption band noted at 1050 cm^{-1} is indicative of the Si-O stretching mode and revealed that SiO_2 is the predominant component in the film.

To test the adhesion strength of the films, peel adhesion ("Scotch tape") tests were performed.¹² This technique measures the threshold value of the film-substrate bond strength, above which the film is peeled away. After performing the peel adhesion test on a number of samples, it was found that thinner films (less than 1000 Å thick) were more adherent to the composite surface than were the thicker films (generally greater than 2000 Å thick), perhaps due to a greater degree of intrinsic stress. Composite samples deposited with SiO_2 films of thickness greater than 1000 Å and which would otherwise not pass the peel adhesion test were subjected to ion implantation in the Ohio University accelerator facility.

Using a micropositioning system, small areas (2-3 mm^2) of the samples were exposed to a 3.0 MeV beam of He^{2+} ions with a beam current 20-60 nA for various lengths of time (30 min - 2 hours). The result is a variation by a factor of two in He^{2+} fluences between adjacent sites. Preliminary results show that the implanted region of the film passed the peel adhesion test, but areas outside of that region did not. Figure 2 is a diagram indicating the result after a 2 hour dose of He^{2+} ions. Pending more detailed investigation, it is safe to conclude at this point that ion implantation under these conditions enhances the adhesion of the film to the substrate.

¹²ASTM D 3330-83, 3359-83

Several coated, but not ion implanted, samples were also tested for their ability to resist oxidation by exposing them to high temperatures (to 400°C) in an ambient environment for different lengths of time. (At present, ion implantation can only be performed readily over small surface areas. Once improved adhesion is established, implantation over larger areas will be attempted.) Uncoated samples were also tested for comparison. The masses of the samples were monitored at regular intervals for up to 300 hrs at several temperatures in the range 390-400°C. Preliminary findings indicate that the coatings were effective against oxidation under these temperature conditions. The weight loss after exposure of the coated sample was significantly lower than that of the uncoated one (Figure 3). While reduced, oxidation was not eliminated. This could be due to oxidation through cracks in the coating, or, more likely, oxidation at the edges and corners of the sample.

II.D. Conclusions

Ion implantation improves adhesion of SiO₂ films to polyimide composite. Additional work to determine the minimum implantation dose and energy is needed to find the optimum conditions for adhesion improvement.

III. SILICA AS OXYGEN BARRIER COATING

III.A. Introduction

Oxidation protection of a material by the application of a protective coating requires that the coating itself be immune to oxidation. In general, ceramic materials, such as silicon dioxide, silicon carbide, and silicon nitride, are highly oxidation resistant, even to temperatures as high as 1300°C.^{13,14} Ceramics have been successfully applied as oxidation resistant coatings to metals, other ceramics, and carbon-carbon composites. Amorphous silica has been deposited by the plasma enhanced chemical vapor deposition (PECVD) process onto nickel-based superalloys and has been shown to significantly reduce the degree of oxidation of these materials at temperatures above 1000°C.¹⁵

A significant amount of work has been done in the area of oxidation resistant coatings for space applications. For example, the prevention of atomic oxygen attack on space borne solar mirrors and

¹³M. Maeda, K. Nakamura, and N. Azuma. J. Ceram. Soc. Japan **96** 795 (1988).

¹⁴ibid., p. 1028

¹⁵M. J. Bennet, A. T. Tuson, C. F. Knights, and C. F. Ayers. Mat. Sci. Technol. **5** 841 (1989).

photovoltaic array blankets has been accomplished by the application, by a variety of different techniques, of coating materials such as silicon dioxide and aluminum oxide.^{16,17,18}

In the present study, a near-stoichiometric SiO₂ film was deposited onto a composite surface from an organosilicon precursor (tetraethylorthosilicate) by the plasma enhanced chemical vapor deposition (PECVD) technique described above. Tetraethylorthosilicate (TEOS) was chosen as the source material because of its non-toxic and non-hazardous nature and its ease of handling versus other common silicon sources, such as silane. Also, TEOS contains sufficient oxygen to allow the formation of stoichiometric silicon dioxide by pyrolytic and plasma-induced decomposition without the need to supply additional oxygen.

III.B. Experimental Procedure

The deposition of SiO₂ films onto polyimide composite surfaces was performed in the PECVD reactor described above. Silicon wafer pieces and polyimide composite samples (2 cm square) were placed horizontally on the heater. The silicon wafers served as witness coupons for characterization of process parameters.

Tetraethylorthosilicate (Aldrich, 99.999%) was placed in a glass bubbler and heated to 60°C to enhance vaporization of the liquid (b.p. 168°C). As the carrier gas, argon was introduced into the bubbler, and the entrained vapor was carried to the reaction chamber through 0.25" diameter stainless steel tubing which was wrapped with heating tape to maintain 60°C throughout to prevent condensation of TEOS vapor inside the tubing. The Ar flow rate was monitored and controlled by passing the gas through a rotameter installed in the line. The pressure was controlled by a throttle valve and was measured by a thermocouple gauge located downstream from the chamber.

III.C. Results and Discussion

The refractive indices (n) of the films match closely to that of thermally grown SiO₂ (1.46). Although only a few samples were analyzed, covering the deposition temperature range of 268°C to 390°C (measured as the temperature of the heater surface; the temperature of the substrate surface itself averaged approximately 10°C less than the heater surface), behavior similar to that seen previously was observed. This behavior is an increase in refractive index with increasing temperature to a point (in the present case, 300°C), followed by a decrease at still higher temperatures.

¹⁶D. A. Gulino, R. A. Egger, and W. F. Banholzer. J. Vac. Sci. Technol. **A5** 2737 (1987).

¹⁷D. A. Gulino. Adv. Mat. and Manuf. Processes. **3** 261 (1988).

¹⁸B. A. Banks, M. J. Mirtich, S. K. Rutledge, D. M. Swec, and H. K. Nahra. NASA TM-87051 (1985).

From the refractive index, the film densities (Table III) were calculated using the Clausius-Mossotti (CM) relationship:¹¹

$$\rho = \frac{k(n^2 - 1)}{n^2 + 2}$$

where ρ is the density and k is a constant equal to 8.1148. The value for the constant is obtained empirically from data obtained on thermally grown (920 °C) SiO₂.

A wet etch test was also performed on the SiO₂ films. Upon exposure to a 100:1 H₂O:HF solution, the etch rate was observed to vary between 145 Å and 225 Å per minute. This compares favorably with other reported etch studies¹⁹ and indicates a reasonably dense film with little or no pinholes or other bulk defects.

The deposition rate was found to decrease when the substrate temperature was increased. The trend is similar to that reported elsewhere.^{9,20,21} This behavior may indicate an adsorption-controlled reaction. As the substrate temperature rises, the active species gain kinetic energy; consequently, the probability of adsorption is reduced, and that of desorption is increased. Increasing temperature may also promote surface recombination of the adsorbed precursors, thus causing the negative dependence of the deposition rate with temperature. The apparent heat of adsorption, which is the thermodynamic correspondent for the activation energy of the TEOS-SiO₂ film, was calculated from an Arrhenius plot and found to be 4.1 kcal/mole (17 kJ/mole). This compares very well with an activation energy of 4.7 kcal/mole (19 kJ/mole) reported by Chin and Van de Ven⁹ and in qualitative agreement with a value of 2.6 kcal/mole (11 kJ/mole) reported by Webb, et al.²² In both of these experiments, the investigators used a mixture of TEOS and oxygen as the reactant precursors.

The deposition rate was found to increase with an increase in RF power (Figure 4). With such an increase in power, the plasma density increases with a corresponding increase in the concentration of ions and free radicals formed as a result of TEOS dissociation. This is expected to enhance decomposition of the gaseous TEOS species and lead to a higher deposition rate.

The process total pressure was varied from 300-1000 mTorr (constant residence time), and the deposition rate was found to be affected slightly. This is shown in Figure 5. Two opposing forces interplay as the pressure is increased. As the TEOS partial pressure is increased, the deposition rate is also increased.

¹⁹D. T. C. Huo, M. F. Yan, and P. D. Foo. J. Vac. Sci. Technol. **A9** 2602 (1991).

²⁰W. Kulish, T. Tippman, and R. Kassing. Thin Solid Films **174** 57 (1989).

²¹C.-P. Chang, C. S. Pai, and J. J. Hsieh. J. Appl. Phys. **67** 2119 (1990).

²²D. A. Webb, A. P. Lane, and T. E. Tang. Proc. Electrochem. Soc. **89** 571 (1989).

Consequently, reduction of the effective diffusivity of the species is likely to change the reaction from the surface-controlled regime to the diffusion-controlled one, and thus dampen the deposition rate.

Several coated samples were tested for their ability to resist oxidation by exposing them to high temperature in an ambient environment for increasing lengths of time. Uncoated samples were also tested for comparison. The masses of samples were monitored at regular intervals for up to 300 hrs at several temperatures in the range 380-400°C. The results indicated that the coatings were effective in preventing thermo-oxidative mass loss under these atmosphere and temperature conditions. The weight losses after exposure of the coated samples were all significantly lower than that of the uncoated one (Figure 6).

The best results were obtained with twice-coated samples (Figure 7). In these cases, one film of 1250-1500Å was applied, the chamber brought to atmosphere, and then the deposition process repeated to apply a second coating directly over the first. A possible explanation for this behavior may be elucidated from studies done by Crowell, et al.^{23,24} They investigated the fundamental mechanism of SiO₂ film growth from TEOS onto SiO₂ surfaces, and found that partial dissociation of the TEOS molecule occurs upon adsorption to the SiO₂ surface, leaving two-to-three ethoxy ligands per reaction site. This adsorbed species then decomposes to form SiO₂ by beta-hydride elimination. They also point out the involvement of hydroxyl groups in the initial reaction of TEOS with the SiO₂ surface. Thus, consumption of hydroxyl groups to produce adsorbed siloxane on SiO₂ surfaces is a possible mechanism and is likely to produce more uniform coverage for the second film.

As a check, polyimide composite samples were heated to 390°C in a nitrogen-only atmosphere at a pressure of 0.01 Torr. A small amount of mass loss (less than 1%) was observed after 200 hours. This is likely due to the loss of volatile impurities, but overall indicates that the composite is not subject to pyrolytic decomposition at this temperature.

It is important to note that oxidation of the coated samples was not altogether eliminated, and this is likely due to oxidation at the edges or corners of the samples. Current efforts are directed to further improve the coating of the deposited sample so that better oxidation resistance is achieved.

III.D. Conclusions

Near stoichiometric silicon dioxide films were deposited from tetraethylorthosilicate by PECVD onto silicon wafer and polyimide composite substrates. The growth rate of the films was correlated with process parameters and was found to proceed by an adsorption controlled reaction mechanism, which is substantiated by the observation that the deposition rate decreased as the substrate temperature was increased. At

²³J. E. Crowell, L. L. Tedder, H. C. Cho, F. M. Cascarano, and M. A. Logan. *J. Vac. Sci. Technol.* **A8** 1864 (1990).

²⁴J. E. Crowell, H. C. Cho, F. M. Cascarano, and L. L. Tedder. *Proc. Electrochem. Soc.* **90-7** 215 (1991).

thicknesses ranging from 2500 - 3500 Å, the films provided significant thermo-oxidative protection to polyimide composites at temperatures of 390-400°C.

IV. MULTILAYER COATINGS

IV.A. Introduction

In this study, dual layer coating systems consisting of SiO_2 and Al_2O_3 were deposited by PECVD onto PBCs, and the durability of the PBCs at elevated temperature was measured and compared to that of uncoated material.

Aluminum oxide has already been looked at for similar applications both by Harding²⁵ under the NASA HITEMP program and by McClure at the 3M Company.²⁶ In the former study, alumina was deposited from aluminum tri-isopropoxide onto neat polyimide (PMR-15) by CVD at 300–450°C. To reduce stress at the polymer/alumina interface, a compliant layer consisting of a high temperature polymer, such as NR-150 or PMR-II-50, was used. The compliant layer is chosen such that its coefficient of thermal expansion (CTE) is intermediate between that of the substrate and the coating to accommodate the induced thermal stresses in the film upon cooldown. Harding found that subsequent exposure of the coated polyimide to ambient atmosphere at 316–343°C for 200–300 hours resulted in reductions in mass loss over an equivalent, uncoated sample. The mass loss reductions ranged from 50% for a sample without a compliant layer to 500% for a sample whose alumina coating was preceded by a complaint material at the interface.

In the latter study, McClure looked at alumina as both a protective layer and an adhesion promoter in a four-layer coating system once proposed for Space Station Freedom solar dynamic power system mirrors. The motivation for the use of two dissimilar materials was three-fold. First, the Al_2O_3 was found to be a good adhesion promoter to the graphite-epoxy composite substrate. Second, the Al_2O_3 is actually more resistant to oxygen penetration than the SiO_2 , while the SiO_2 was thought to provide better moisture resistance. Thus, the two-coating system provides both good oxygen resistance and good moisture resistance. Third, the use of two dissimilar but compatible materials aids in the covering of pinhole defects. The likelihood that the second overlayer will cover pinholes in the first layer is greatly enhanced when the second layer is a different material.

In the present study, Al_2O_3 and SiO_2 films were deposited by the PECVD technique. No interfacial compliant layer was used, and the substrates consisted of samples of PMR-15 and PMR-30-based carbon

²⁵D. R. Harding in HITEMP Review 1991: Advanced High Temperature Engine Materials Technology Program. NASA CP-10082, 1991, pp. 10-1 to 10-10.

²⁶D. J. McClure. NASA CR-4158, July 1988.

fiber composites provided by the Polymers Branch at the NASA Lewis Research Center. Aluminum tri-isopropoxide (ALI) was used as the source gas for Al_2O_3 depositions and tetraethoxysilane (TEOS) was used as the source gas for SiO_2 depositions. Characterization of this dual layer system consisted of examining the effectiveness of various thicknesses of each of these two materials on the thermo-oxidative stability of PBC substrates.

IV.B. Experimental Procedure

Deposition of both Al_2O_3 and SiO_2 films onto polyimide composite surfaces was performed in the PECVD reactor described above. For Al_2O_3 depositions, aluminum tri-isopropoxide (Aldrich) was heated to 120°C in an oil bath, and for SiO_2 depositions, tetraethoxysilane (Fisher) was heated to 75°C . In both cases, argon, as the carrier gas, was introduced into the bubbler, and the entrained vapor was carried to the reaction chamber through 6.3 mm ($\frac{1}{4}$ ") diameter stainless steel tubing which was wrapped with heating tape to prevent condensation of ALI or TEOS vapor inside the tubing. The Ar flow rate was monitored and controlled by passing the gas through a rotameter installed in the line. The pressure was controlled by a throttle valve and was measured by a thermocouple gauge located downstream from the chamber. Pressures during deposition were approximately 0.9 Torr.

IV.C. Results and Discussion

Figure 8 presents the results of this experiment in which a variety of coating thickness combinations were examined. In terms of preventing thermo-oxidative degradation at 380°C , the three best coating systems all contained 1500 Å of Al_2O_3 . Figure 9 presents the data of Figure 8, but grouped by keeping the thickness of one or the other layer constant. Presenting the results in this way makes more clear the effectiveness of the 1500 Å Al_2O_3 layer. In both cases, the best performing dual layer system was one in which a 1500 Å layer of Al_2O_3 was used as the underlayer.

Figure 10 presents the ending (after 320 hours) fractional mass change as a function of total coating thickness. This presentation neglects the fact that the total coating thickness consists of two different materials. Not surprisingly, the greater the thickness, the less mass is lost. The best protection was afforded to those samples total coating thickness exceeded 2500 Å. For this particular batch of substrates, an essentially linear relationship exists between these two variables, at least through the highest total thickness studied.

IV.D. Conclusions

Dual layer thin film coatings consisting of an Al_2O_3 underlayer and a SiO_2 overlayer have been investigated as oxygen barriers for polyimide-based composite at elevated temperatures. While all coatings

systems studied protected the composite substrate to some extent, the best results were obtained with thick coatings (2500 – 3500 Å) where the Al_2O_3 underlayer thickness was at least 1500 Å.

V. SUMMARY AND FUTURE WORK

The three-year effort summarized in the preceeding pages produced significant and useful results. We have identified ion implantation as a promising technique for improving the adhesion of silica films to polyimide substrates. Additional work is required to enlarge the surface area that can easily and economically be implanted.

We have identified SiO_2 as a promising coating material for thermo-oxidative protection of polyimide-based composites. We also looked at Al_2O_3 separately and in combination with SiO_2 , but these have not duplicated the best results we ever obtained, which were with samples consisting of two layers of SiO_2 applied in separate steps.

The problems which remain are concerned with the difficulty in obtaining repeatable performance from uncoated substrates and the problems which arise when attempting to protect the cut edges of machined parts. In addition, further studies are needed both to determine the effect of longer term exposure on the mechanical properties of PBCs and the effect of a harsher environment (e.g., higher pressures, thermal cycling) on the durability of the coatings.

VI. ACKNOWLEDGMENTS

I would like to thank the National Aeronautics and Space Administration, the Lewis Research Center, and the Polymers Branch headed by Dr. Michael Meador for their support over the last three years and for permitting us be a part of their research efforts in this very interesting area.

FIGURE CAPTIONS

- Figure 1. Schematic diagram of deposition system used for all depositions of Al_2O_3 and SiO_2 .
- Figure 2. Demonstration of the observed effect of ion implantation on the adhesion of SiO_2 to polyimide. By use of the peel adhesion test, regions implanted with He^{+2} were found to more adherent than surrounding regions.
- Figure 3. Fraction of original mass vs. exposure time for SiO_2 -coated polyimide composite exposed to elevated temperature. An improvement in thermo-oxidative durability was noted.
- Figure 4. Effect of RF power on deposition rate of SiO_2 .
- Figure 5. Effect of total pressure on the deposition rate of SiO_2 .
- Figure 6. Effect of a variety of thickness of SiO_2 coatings on the thermo-oxidative durability of polyimide composite.
- Figure 7. Thermo-oxidative durability of polyimide composite samples "twice-coated" with SiO_2 . This was the best performance ever achieved for polyimide composite sample coated with either an Al_2O_3 or SiO_2 coating.
- Figure 8. Thermo-oxidative durability of polyimide composite samples coated with both Al_2O_3 and SiO_2 . The notation indicates first the thickness of Al_2O_3 in 100s of Å followed by the thickness of SiO_2 , also in 100s of Å.
- Figure 9. Data shown in Figure 8 but replotted to hold the thickness of either Al_2O_3 (left) or SiO_2 (right) constant.
- Figure 10. Comparison of total coating thickness (sum of SiO_2 and Al_2O_3 thicknesses) on ending fractional mass change.

TABLE I. Base Conditions for SiO₂ Deposition from TEOS.

System Pressure:	300 - 1000 mTorr
Substrate Temperature:	265 - 425 °C
Gas Composition:	TEOS + Argon
Frequency:	13.56 MHz
RF Power:	75 - 140 Watt
Carrier Gas flow rate:	180 - 250 sccm

TABLE II. Process Conditions For SiO₂ Film Preparation from TEOS by PECVD.

Substrate Temperature (°C)	Pressure (mTorr)	Carrier gas (Ar) flow rate (sccm)	Deposition Rate (Å/min)	Uniformity variation (%)
265	1000	200	215	8.20
300	1000	200	165	24.50
300	800	220	150	6.74
300	600	250	135	11.60
300	400	200	40	13.40
300	300	180	31	15.60
320	800	250	167	4.80
340	800	200	175	2.60
390	1000	220	123	11.38
425	1000	250	80	22.4

Table III. Calculated densities of several SiO₂ films.

n (600 nm)	Dep. Temp (°C)	ρ (gm/cm ³)
1.4611	268	2.227
1.4672	300	2.252
1.4615	390	2.229

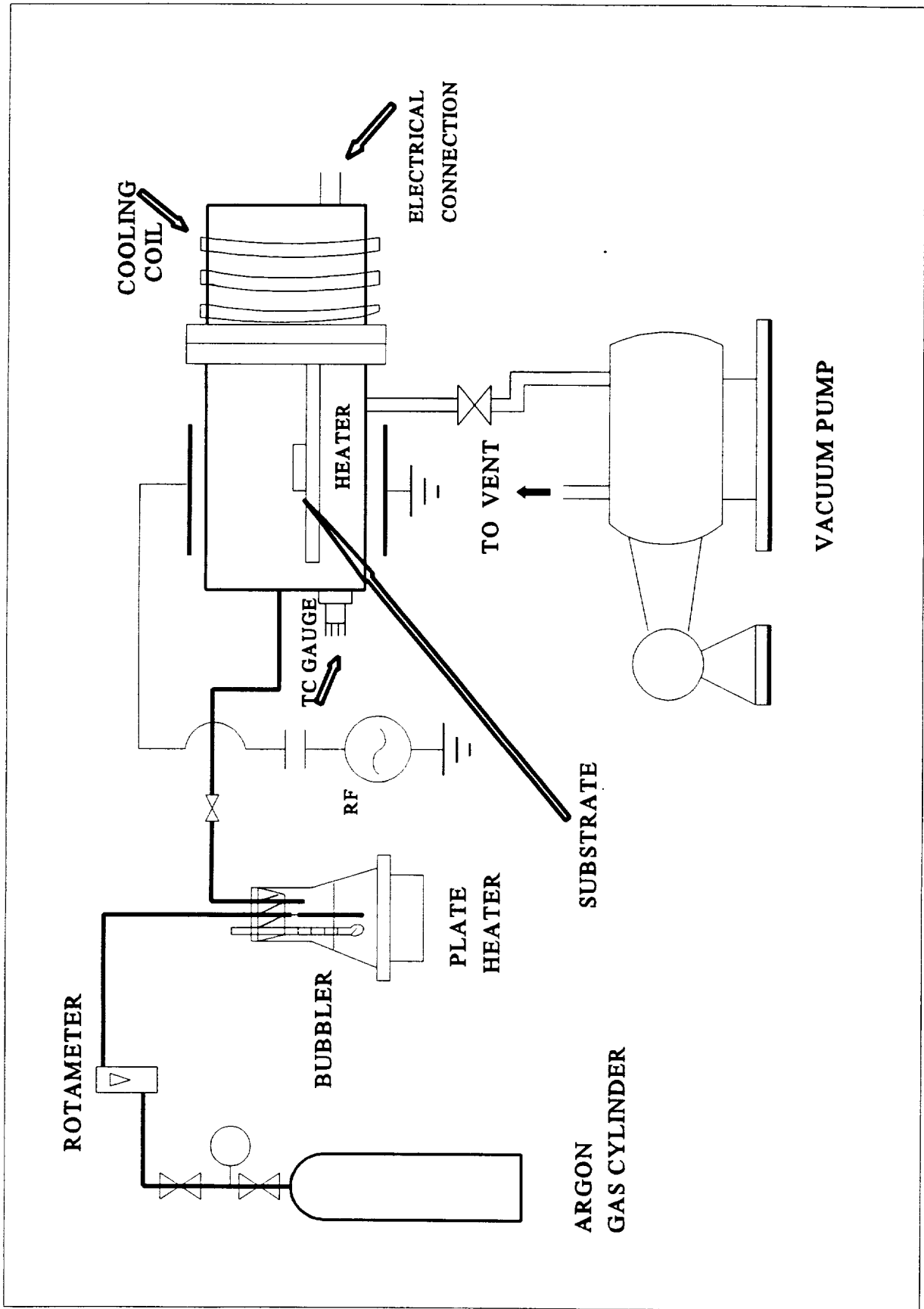
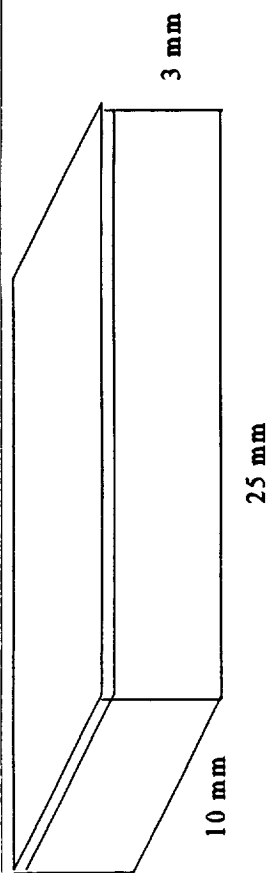
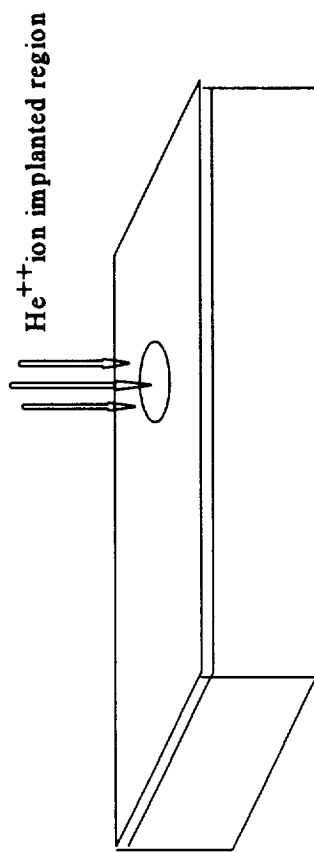


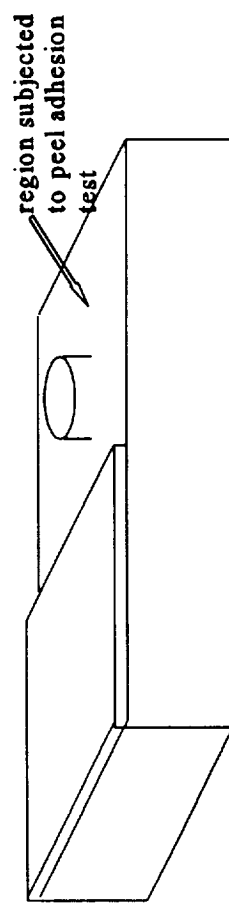
Figure 1



a) SiO₂ coating 3000 Å thick on PMR-15 polyimide



b) Ion implantation over region 2 mm in diameter



c) After peel adhesion test on right side, only ion implanted region remains

Figure 2

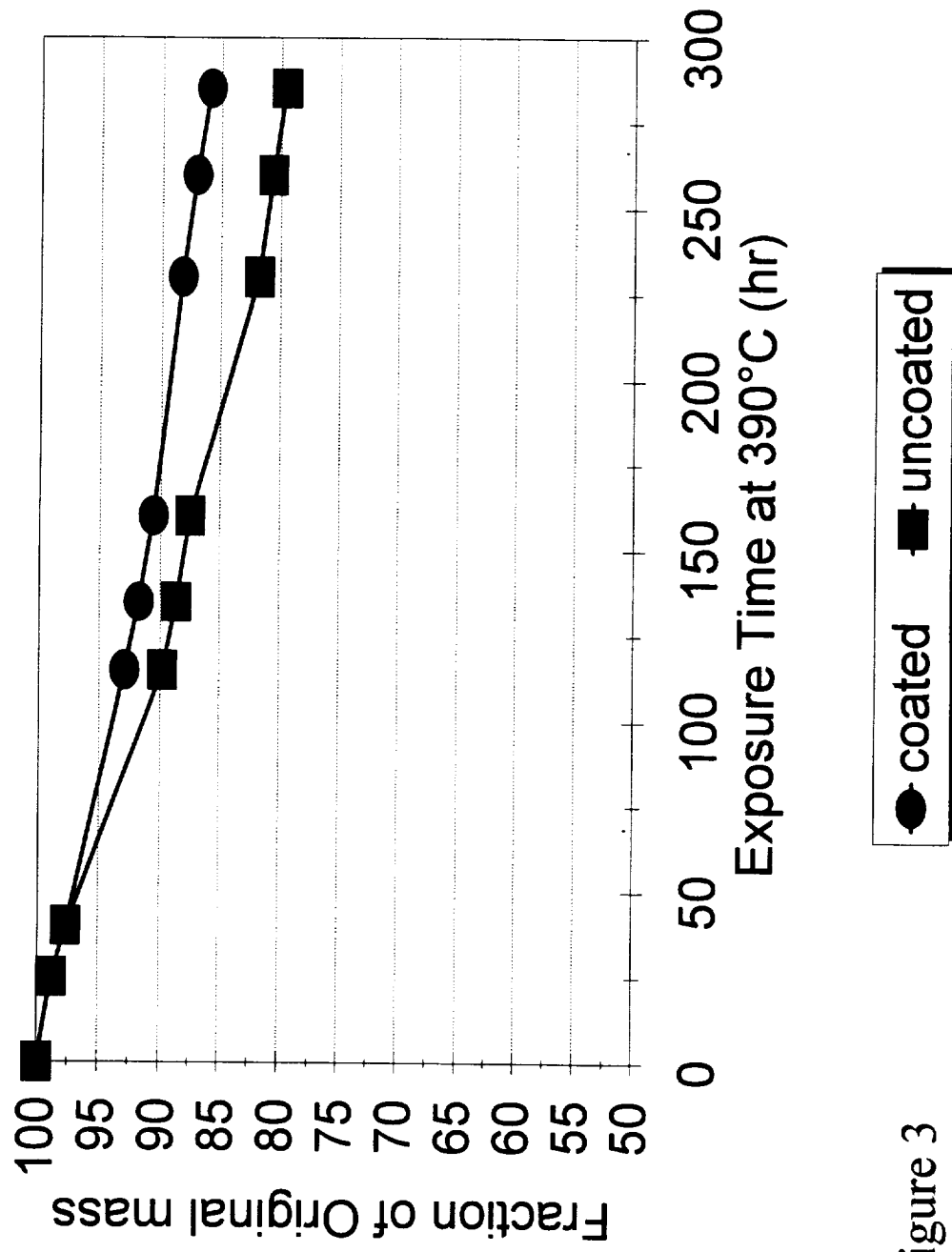


Figure 3

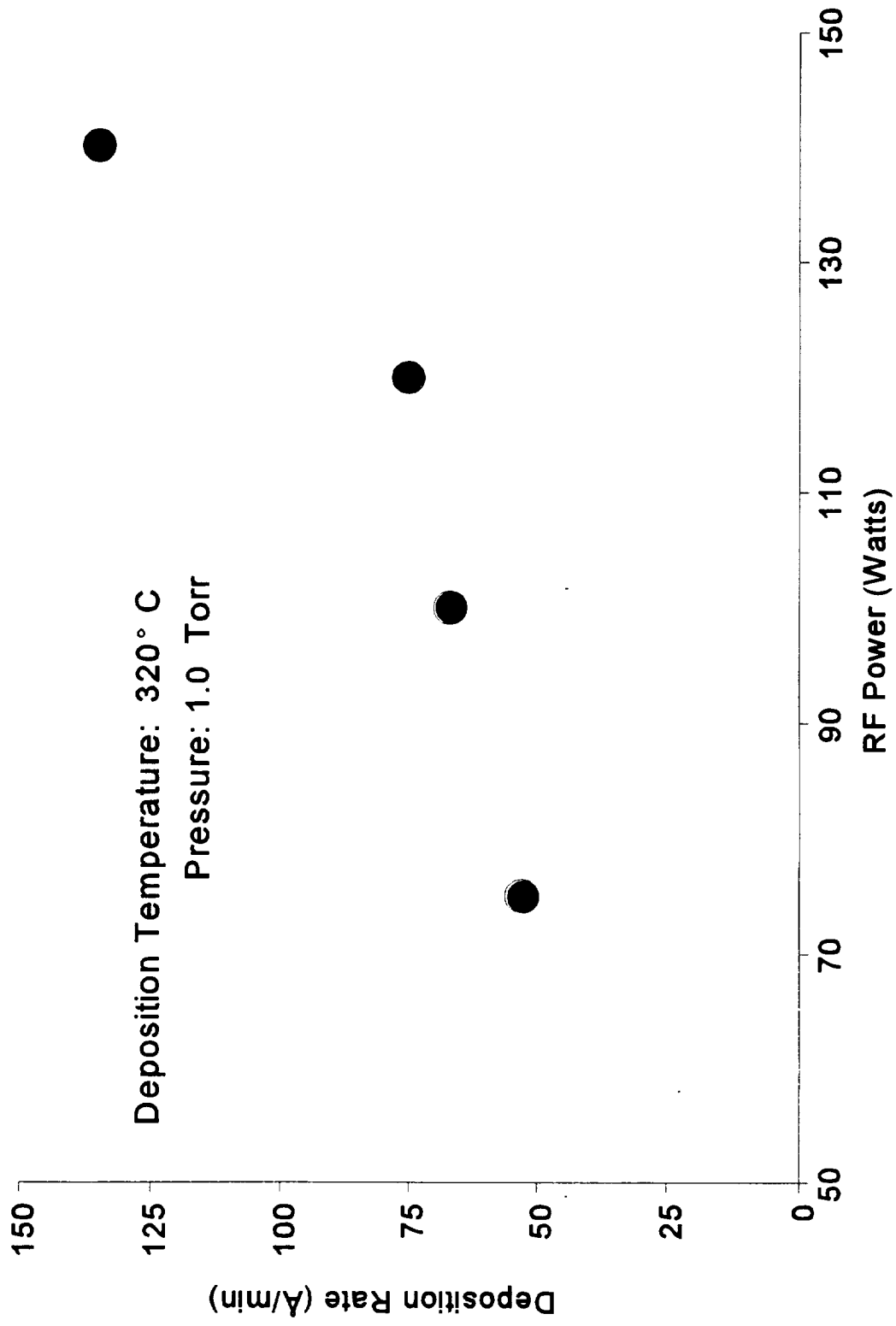


Figure 4

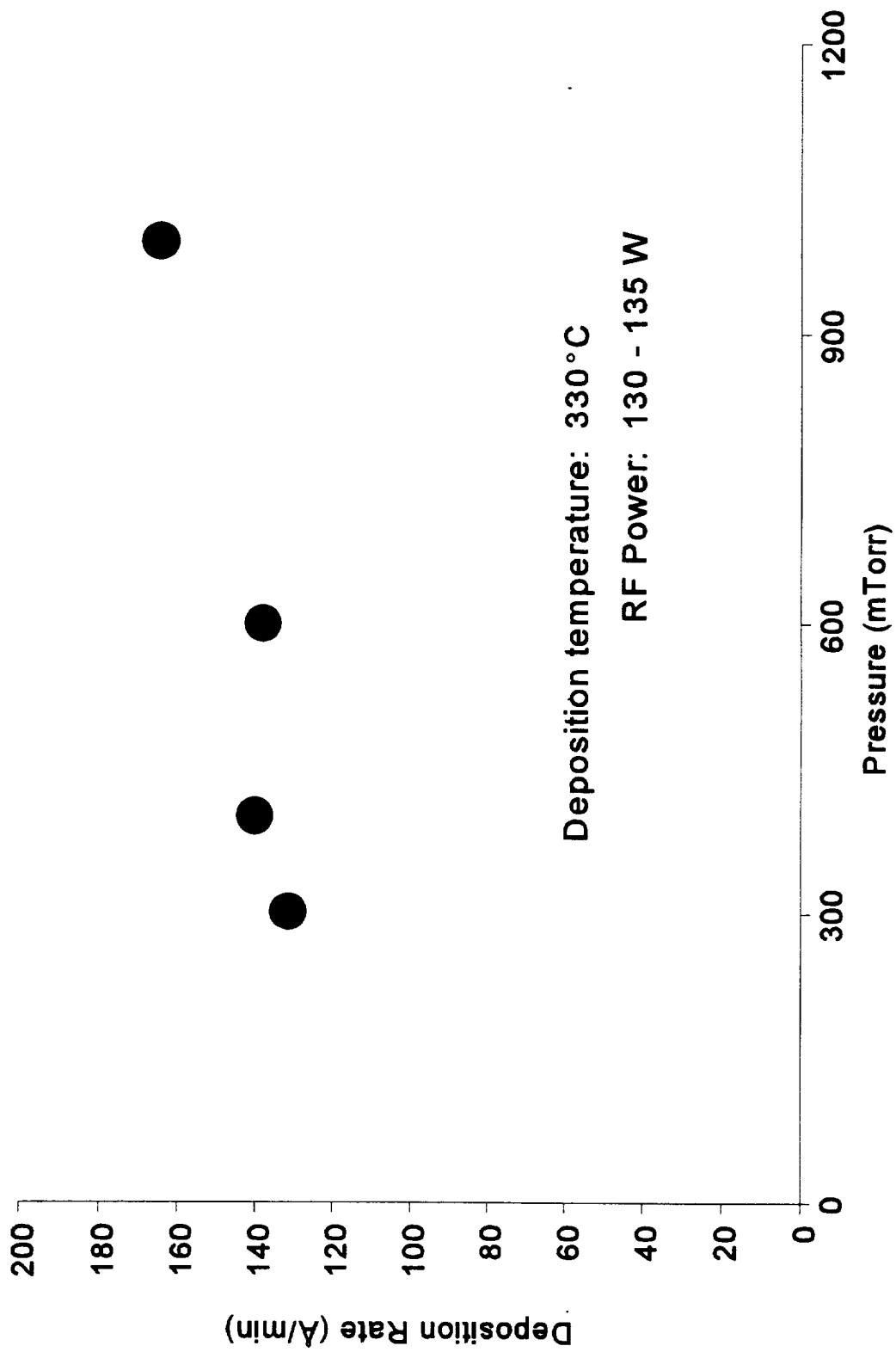


Figure 5

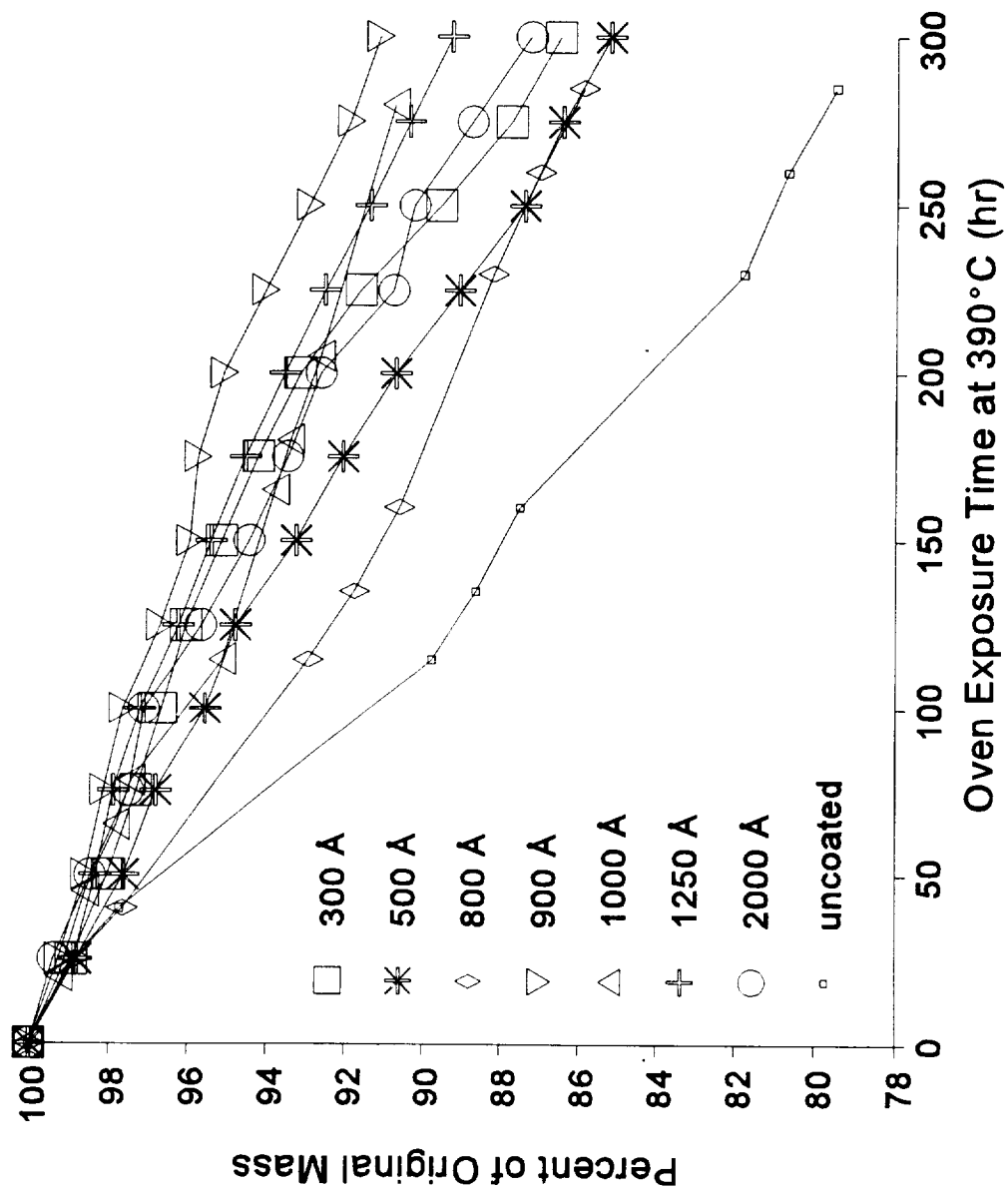


Figure 6

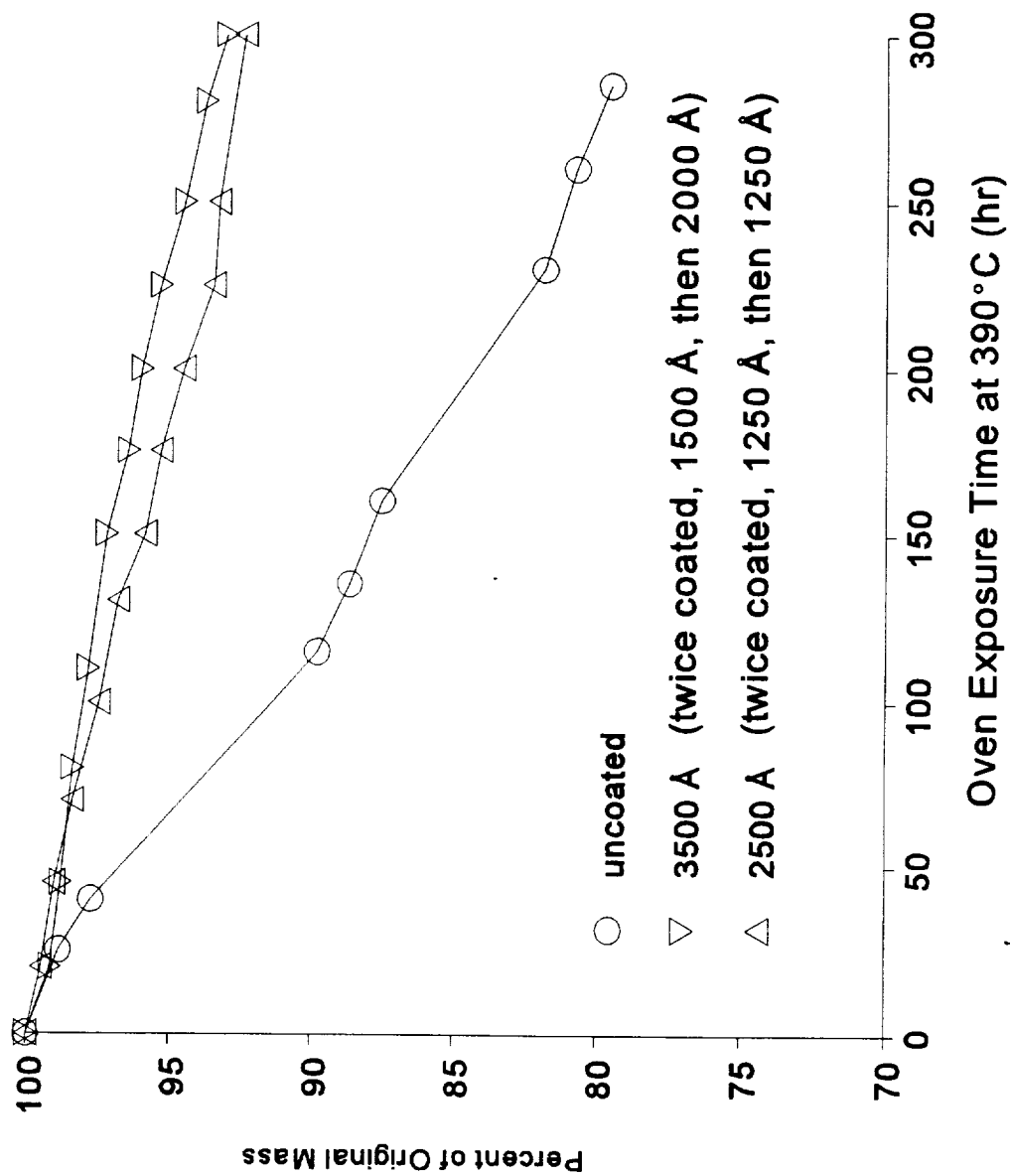


Figure 7

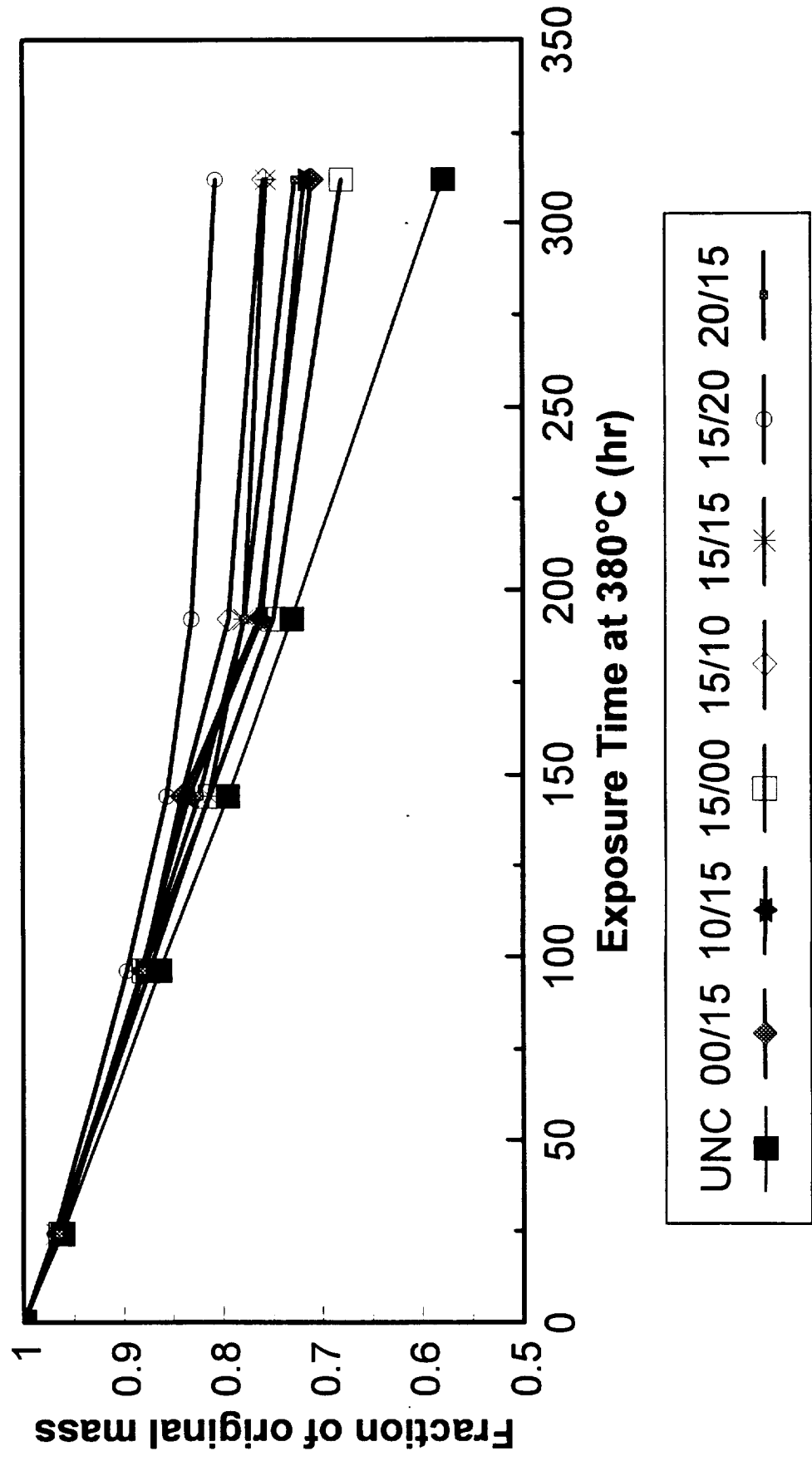
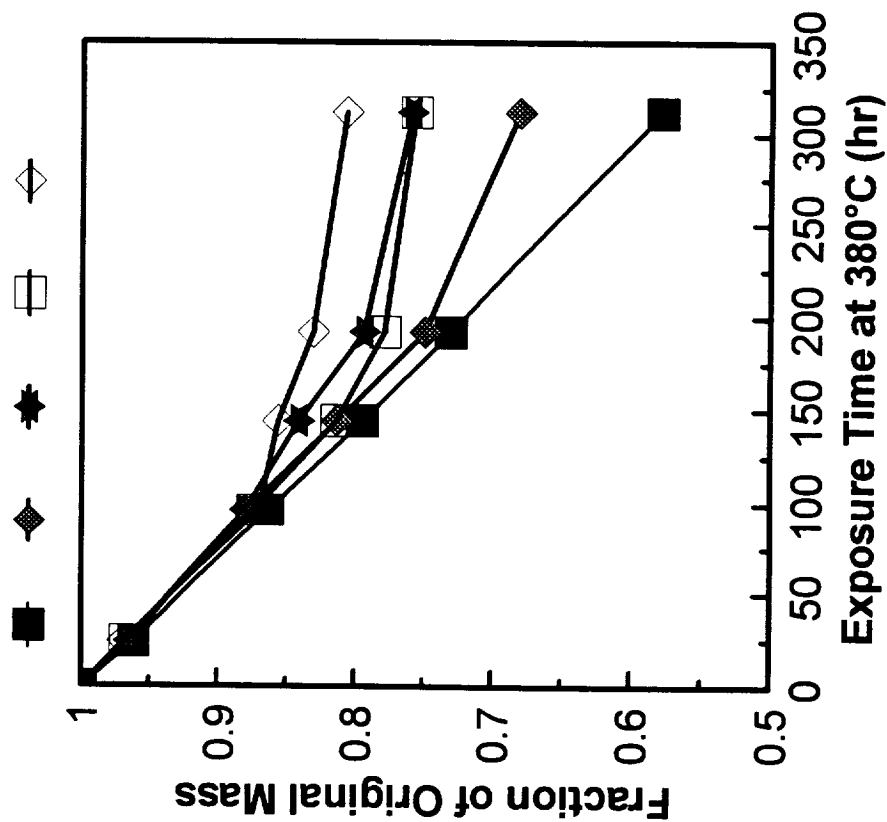


Figure 8

Constant Al₂O₃ Thickness (1500Å)

UNC 15/00 15/10 15/15 15/20



Constant SiO₂ Thickness (1500Å)

UNC 00/15 10/15 15/15 20/15

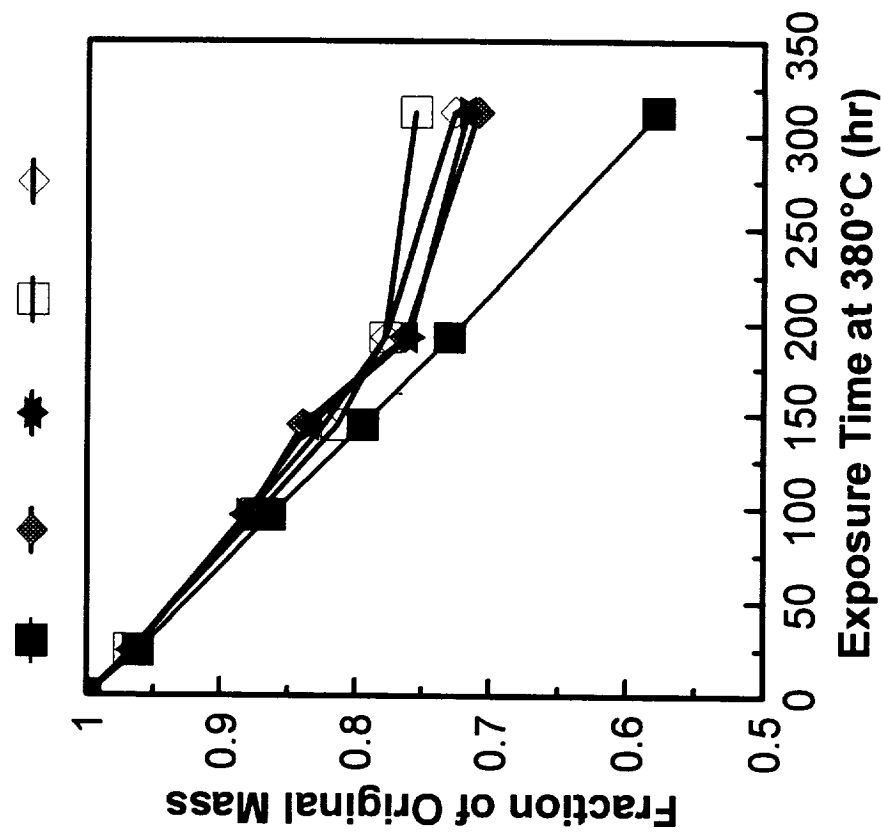


Figure 9

Comparison of Total Coating Thickness

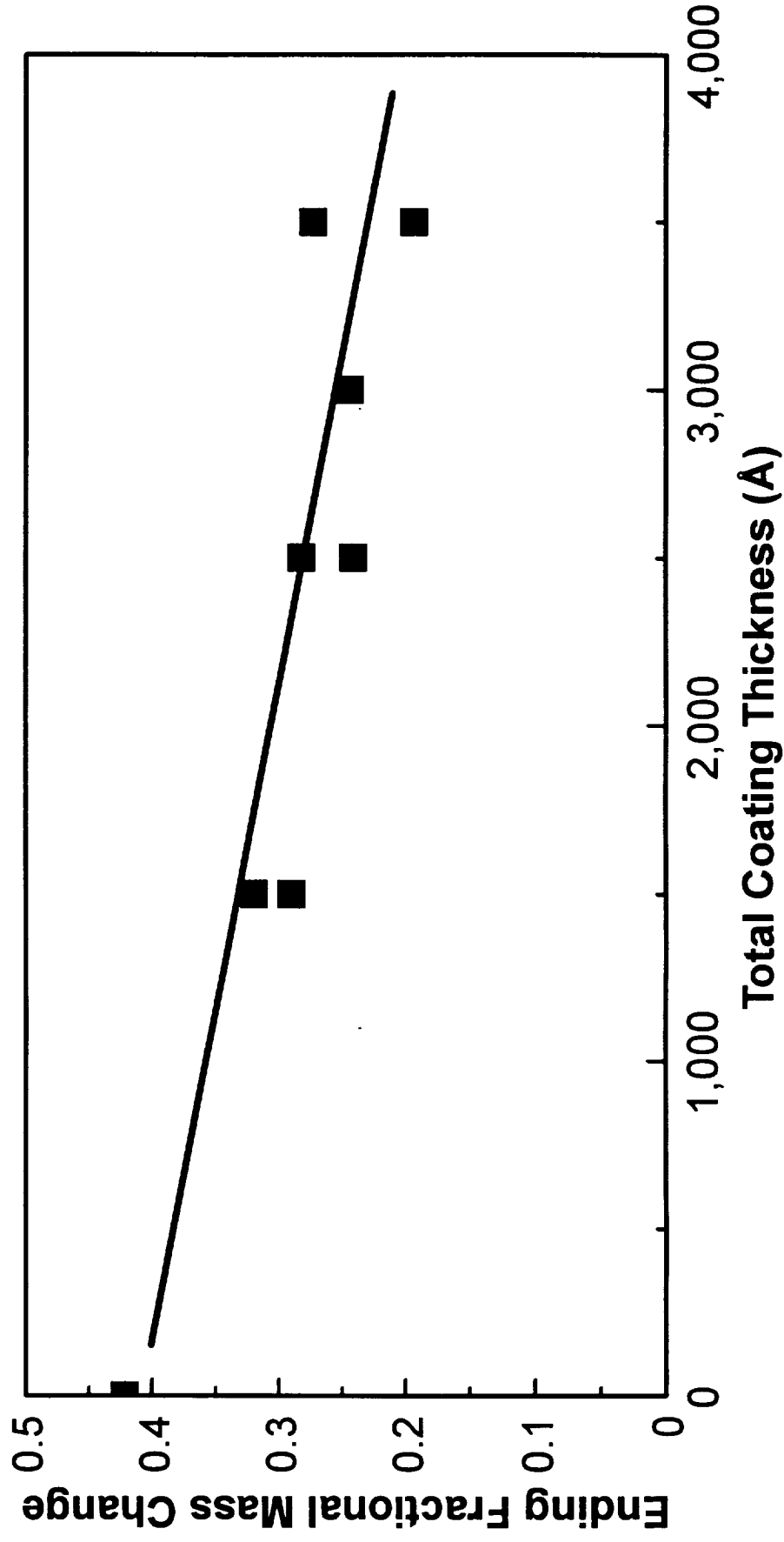


Figure 10

